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PICOSECOND LASER STUDIES OF EXCITED STATE PROTON TRANSFER.(U)
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>Picosecond laser techniques were both used and developed to obtain new information on ultrafast molecular processes in liquids. From these studies, primarily of organic molecules, we have gained insight into: the physical and chemical pathways by which excited state molecules dissipate their energy by proton and electron transfer phenomena, the nature of intermolecular motions (cage effects in chemical reactions) and intramolecular motions,</p>					

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about methylene groups, photodissociation of excited molecules and energy relaxation in the fragments generated, e.g. diphenylcarbene, the photoionization and subsequent electron solvation dynamics of pyrene in alcohols. The information we have obtained has important implications in the photostability of dye lasers and polymer systems, the development of new lasers based on the generation of large excited state populations in transient species, and the general effects of intense lasers on materials.

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A

"Picosecond Laser Studies of Electron-Hole Interactions and Double Proton Transfer", K. Gnädig, W. Hetherington, M. Crawford, R. Micheels and K.B. Eisenthal, in Picosecond Phenomena, eds. C.V. Shank, E.P. Ippen and S.L. Shapiro, Springer-Verlag, 1978.

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"Picosecond Laser Studies of the Photodissociation of I₂-Aromatic Complexes and the Formation of I Atom-Aromatic Complexes in Solution", C.A. Langhoff, K. Gnädig and K.B. Eienthal, Chemical Physics, 46, 117 (1980).

"Picosecond Laser Studies of Electron Solvation in Alcohols", Y. Wang, M.K. Crawford, M.J. McAuliffe and K.B. Eienthal, Chemical Physics Letters, 74, 160 (1980).

"Intramolecular Excited-State Charge-Transfer Interactions and the Role of Ground-State Conformations", Y. Wang, M.K. Crawford and K.B. Eienthal, Journal of Physical Chemistry, 84, 2696 (1980).

"Dynamics and Energetics of the Singlet-Triplet Interconversion of Diphenylcarbene", K.B. Eienthal, N.J. Turro, M. Aikawa, J.A. Butcher, Jr., C. Dupuy, G. Hefferon, W. Hetherington, G.M. Korenowski and M.J. McAuliffe, Journal of the American Chemical Society, 102, 6563 (1980).

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"Photodissociation of Diphenyldiazomethane and Energy Relaxation in the Diphenylcarbene Fragment", C. Dupuy, G.M. Korenowski, M. McAuliffe, W. Hetherington and K.B. Eienthal, accepted for publication by Chemical Physics Letters.

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

A primary objective of this research has been the development and application of picosecond laser methods to the study of ultrafast molecular processes in liquids. Using the techniques of picosecond spectroscopy we have obtained new information on: the physical and chemical pathways by which molecules in excited electronic states dissipate their electronic energy, intramolecular and intermolecular motions in liquids, and the properties of short-lived fragments generated by the laser photoexcitation of the original ground state molecules.

In particular we have investigated: (1) the role of excited state proton transfer in the photostability of ortho-hydroxybenzophenone and in the tautomerization of 7-azaindole dimers, (2) intramolecular motions and electron transfer in hooked together donor and acceptor molecules, (3) photodissociation of iodine, I_2 , complexed with aromatic molecules, the subsequent iodine atom reaction with aromatic molecules, and cage effects, (4) photodissociation of diphenyldiazomethane and energy relaxation in the important chemical intermediate, diphenylcarbene and (5) photodissociation of pyrene in alcohols, the solvation dynamics of the ionized electron, and insight provided by this work on energy deposition in pulse radiolysis experiments. We have used

picosecond fluorescence, laser-induced fluorescence and a new technique combining a laser-triggered flash lamp with a streak camera to obtain transient absorption with pico-second resolution, extending for nanoseconds, in one firing of the laser.

AFOSR Program Manager: Dr. Anthony Matuszko

FINAL REPORT OF RESEARCH ACCOMPLISHMENTS

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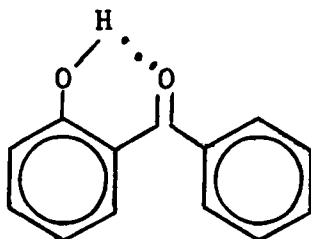
The research supported by this contract has provided new insights into photophysical and photochemical processes in condensed media. Using picosecond laser methods we monitor the various channels by which photoexcitation energy is used to effect physical and chemical changes in molecular systems. We employ the laser not only to probe the properties of the originally excited molecules but to generate new short-lived chemical species which are in turn investigated using picosecond laser methods.

Specifically we have studied the key role played by proton and electron transfer in excited energy relaxing and structure changing phenomena, energy dissipation by photodissociation and photoionization leading to reactive intermediate species, and the development and refinement of general picosecond laser techniques for the study of very rapid molecular processes.

I. Intramolecular Hydrogen Bonding and Photostability

The photostability of ortho-hydroxybenzophenone, OHBP, stands in marked contrast to the high photochemical reactivity of benzophenone, its parent compound. The origin of

this difference is connected to the intramolecular hydrogen bond between the hydroxy proton and the carbonyl oxygen.



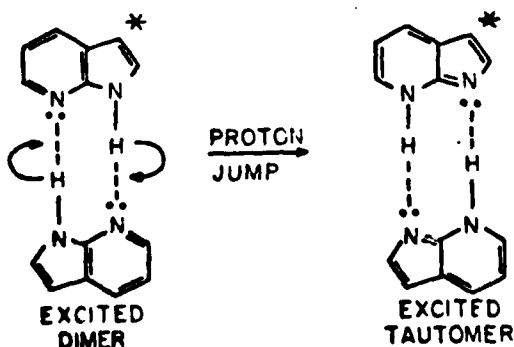
Intramolecular Hydrogen Bond in OHBP

We have used picosecond transient absorption techniques to directly observe and thus support the idea that rapid energy relaxation is responsible for the photostability of OHBP. From our studies we have determined that in a non-hydrogen bonding solvent such as hexane the lack of reactivity is due to rapid energy relaxation within the singlet manifold. The ground state repopulation time is 35 ± 5 ps. No evidence for intersystem crossing to a triplet state was found. In the hydrogen bonding solvent ethanol we find the behavior to be more complicated. Two pathways for energy relaxation from the photoexcited singlet state were observed. One channel leads back to the ground state in roughly 30 ps and the other to a very short-lived triplet state. We established that this state is a triplet state by intermolecular energy transfer and excited state absorption measurements. The

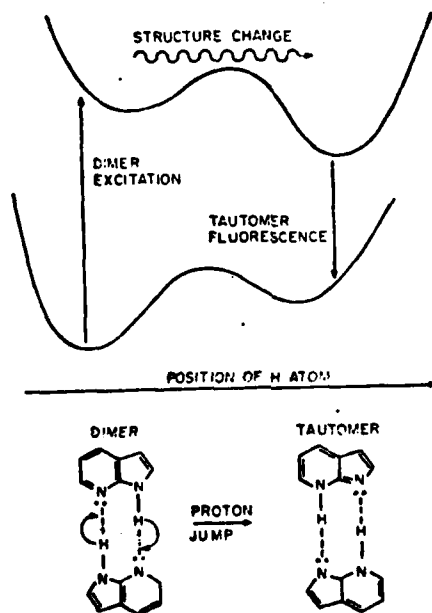
triplet state lifetime is 1.5 ns, which is shorter by a factor of 10^6 than the triplet lifetime of benzophenone in inert solvents. Thus the photostability of OHBP in the hydrogen bond solvent is due to the short duration of its excited state lifetimes, i.e. in both the singlet and triplet states. The disparity between hexane and ethanol can be due to the competitive effects of intra versus inter-molecular hydrogen bonding which can occur in ethanol but not in hexane.

II. Phototautomerization by a Double Proton Transfer Process

A hydrogen bonded system of considerable experimental and theoretical interest in which excited state proton transfer provides a channel for rapid energy relaxation is the dimer of 7-azaindole. Unlike OHBP however the relaxation process effected by the protons does not rapidly return the photoexcited molecule to the ground state. Rather a highly fluorescent excited state tautomer is produced.

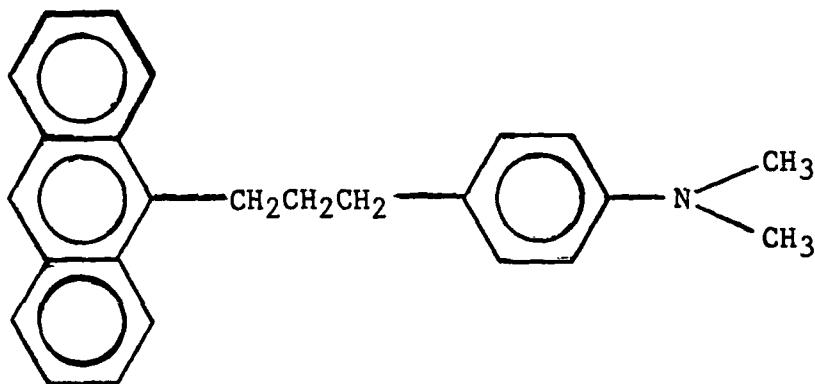


We have used ultraviolet picosecond pulses and a streak camera to monitor the risetime of the tautomer fluorescence and thereby obtain the kinetics of the proton transfer. From our results at room temperature and at 77°k we find that the double proton transfer process is dependent on energy. At room temperature a very rapid tautomerization occurring in less than 5 ps takes place whereas at 77°k both a rapid (5 ps <) and a relatively slow (~1 ns) tautomerization is observed. Carrying out a variety of different experiments we find that a description in terms of a double minimum excited surface explains our measurements of: the rise times of the tautomer fluorescence, the dimer and tautomer excitation spectra, and the temperature dependencies of the dimer and tautomer emissions.



III. Intramolecular Excited State Electron Transfer

In addition to the proton transfer processes we have so far discussed we note that an excited molecule can also relax its energy through intermolecular charge transfer interactions. These interactions can lead to the formation of an exciplex and in suitable solvents to ions. Of particular interest in the work we report here is the role of geometric effects on the dynamics of exciplex formation. We have investigated the hooked together acceptor- $(\text{CH}_2)_3$ -donor system, anthracene- $(\text{CH}_2)_3$ -N,N-dimethylaniline.



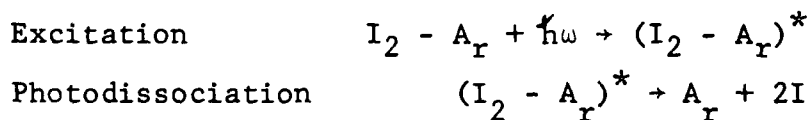
We have used time resolved fluorescence measurements of both the photoexcited anthracene decay and exciplex formation at several wavelengths to monitor the charge transfer dynamics. We have established that there is no intermediate

non-fluorescent state prior to exciplex formation as had been postulated for systems of this type. We conclude that there are severe geometric requirements in nonpolar solvents. If this was not the case then from our intermolecular studies we know that the transfer time at these donor-acceptor separations should be less than 10 ps. We find that the transfer times are in the nanosecond time domain for these hooked together molecules. The observed kinetics for exciplex formation yields the end to end motion of this small chain, (rotation about three methylene groups) and is found to be exponential. This has direct bearing on theoretical models of small chain polymer motions. A very interesting and provoking aspect of this work is our evidence for the presence of two ground state conformers which produce structurally different exciplexes. We find that these excited state structures equilibrate rapidly on the time scale of the exciplex lifetime (126 ns) but slowly on the time scale of exciplex formation (end to end motions) which is in the range of 1-10 ns.

IV. Photodissociation of I₂-Aromatic Complexes and the Reactions of I Atoms with Aromatics

One of the key ways by which electronically excited molecules can dissipate their energy is by the process of photodissociation. We have taken advantage of this energy decay process to investigate a number of elementary processes in liquids. They include (1) the effects of weak ground state complexing on the photodissociation of the I₂ moiety in its complexes with aromatics, I₂-A_r.

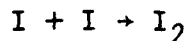
The sequence of steps can be described as follows:



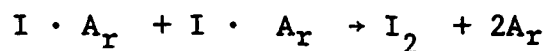
(2) Dynamics of the iodine atom-aromatic reaction characterized by the appearance of a new absorption due to I · A_r



(3) Competition between the I atom reaction with the aromatic as given above in (2) and the cage recombination of the I atoms



(4) The observation of a new cage effect involving iodine atom-aromatic complexes



Our results indicate that the rate of photodissociation of I_2 is not affected by weak binding to the aromatics studied: benzene, mesitylene and xylene. The reaction of the iodine with the aromatic is extremely rapid ($> 2 \times 10^{11} \text{ sec}^{-1}$) and thus dominates the atom cage effect in the neat aromatic liquids. We have indeed observed for the first time the dynamics of a cage effect involving weak complexes. It is the iodine atom-aromatic cage recombination effect in benzene; i.e., the geminate recombination of two $I \cdot B_z$ complexes. Its observation in benzene but not in other aromatic solvents is attributed by us to the higher ionization potential of benzene and thus smaller charge transfer stabilization of the iodine atom-benzene complex relative to the other iodine atom-aromatic complexes. The duration of the iodine atom-benzene, $I \cdot B_z$, cage effect in neat benzene at room temperature is approximately 40 psec.

V. Photoionization of Pyrene and Electron Solvation
in Alcohols

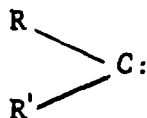
An intense laser pulse can photoionize a molecule by a multiphoton absorption process. In a liquid the photoejected electron is quickly trapped and then solvated. The exact nature of these processes are not known. Similarly the physical and chemical properties of this reactive species, i.e. the solvated electron, are poorly understood. Using our picosecond transient absorption technique which combines a picosecond excitation pulse, a laser triggered flash lamp and a streak camera we have directly measured the dynamics of electron solvation in methanol and ethanol. This work is the first picosecond laser study of electron solvation in liquids which is not pulse-width limited and thus has enabled us to obtain the solvation rate constants. In methanol a value of 17 ps and in ethanol a value of 26 ps are obtained. These times do not closely agree with any of the liquid dielectric relaxation times. Thus contrary to earlier views that the kinetics of the solvation process is simply related to orientational relaxation time is not supported by our work.

One of the exciting findings of this work is the disparities between our picosecond laser results and those obtained in pulse radiolysis experiments. We suggest that

the differences are due to the fundamental process of energy deposition in a pulse radiolysis experiment. In these latter experiments it has been proposed (and hotly contested) that there is significant energy deposition (~ 30 eV) in very small regions ($\sim 20 \text{ \AA}$) called spurs. A comparison with our results, in which there is negligible local energy deposition, leads us to suggest that the higher local "temperatures" in the pulse radiolysis work due to the large local energy deposition, effects a more rapid solvation process and thus shorter solvation times than in the laser experiments. Combining the different results we estimate an effective temperature jump of 32°K for methanol and 16°K for ethanol in the pulse radiolysis experiments. Our results thus directly support the small spur-large energy deposition model in pulse radiolysis experiments.

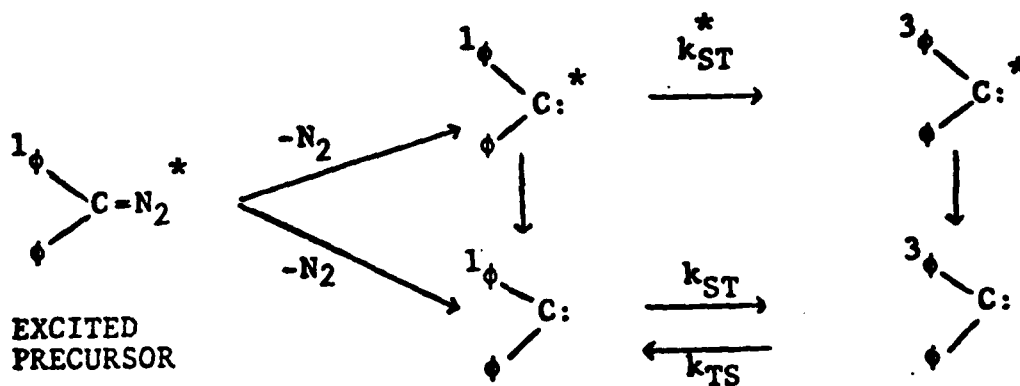
VI. Photodissociation of Diphenyldiazomethane and Energy Relaxation in the Diphenylcarbene Fragment

Although divalent carbon compounds (carbenes), are



an important class of short lived and reactive intermediates, there is little known about the dynamics of their formation

from photoexcited precursors or about the dynamics of energy relaxation in the carbene itself. In order to elucidate the dynamics of carbene formation, energy relaxation, and reaction, an ultraviolet picosecond laser pulse is used to generate diphenylcarbene (DPC) from a diphenyldiazomethane precursor. The sequence of energy decay steps following excitation of diphenyldiazomethane, ultimately leading to diphenylcarbene in its triplet ground state can be written as:



where ϕ represents the phenyl group (C_6H_5) and the superscript $*$ represents excited states. We find that the excited triplet $^3DPC^*$ occurs within 15 ps of photoexcitation. Thus the carbon-nitrogen bond rupture and the subsequent $^1DPC^* \longrightarrow ^3DPC^*$ steps do not individually exceed 15 ps. From the energy of the exciting photon and the energy of $^3DPC^*$ we conclude that the energy of the carbon-nitrogen bond in diphenyldiazomethane is 2 eV or less, a bond value heretofore unknown. Using a laser induced fluorescence method we determined

that the lower singlet to triplet interconversion, k_{ST} , has a value of $9.1 \times 10^9 \text{ sec}^{-1}$. In collaboration with Professor N.J. Turro, who measured the reverse process k_{TS} , we find the equilibrium constant,

$$K = \frac{k_{ST}}{k_{TS}} = \frac{9.1 \times 10^9}{4.1 \times 10^6} = 2.2 \times 10^3$$

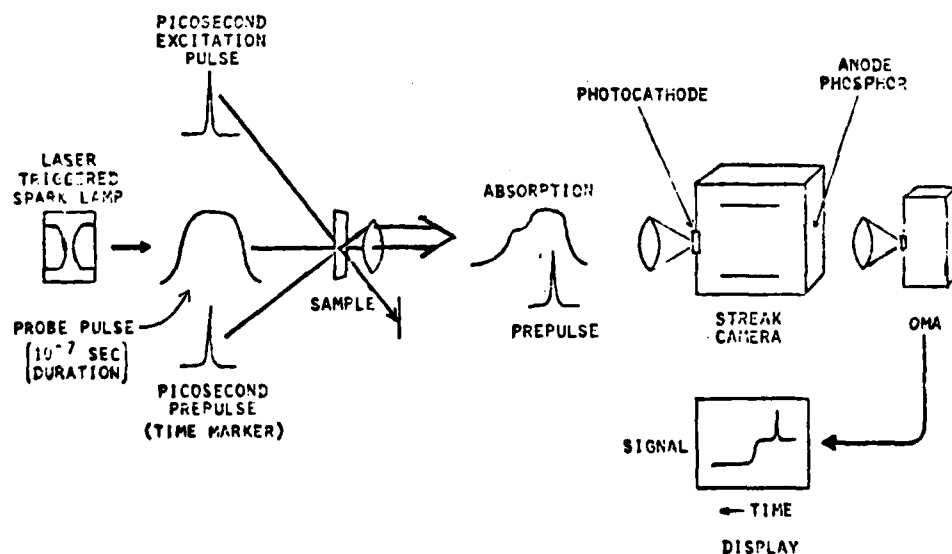
The free energy difference at 25°C is calculated to be $4.6 \pm 0.2 \text{ kcal/mole}$ and after correcting for entropy differences arising from the different multiplicities we obtain an energy separation between the ground triplet and lowest singlet in diphenylcarbene of $3.9 \pm 0.2 \text{ kcal/mole}$.

VII. Picosecond Laser Methods

In such a rapidly moving field as lasers in chemistry, especially picosecond lasers, it is essential to constantly improve and incorporate new methods and the cutting edge of technology in our experimental system. By so doing we and others extend forefront research into new areas of chemistry. To this end and during the period of this contract we have constructed a sophisticated laser, detection and data analysis system to carry out transient absorption and emission experiments. The experimental set-up consists of a Neodymium laser

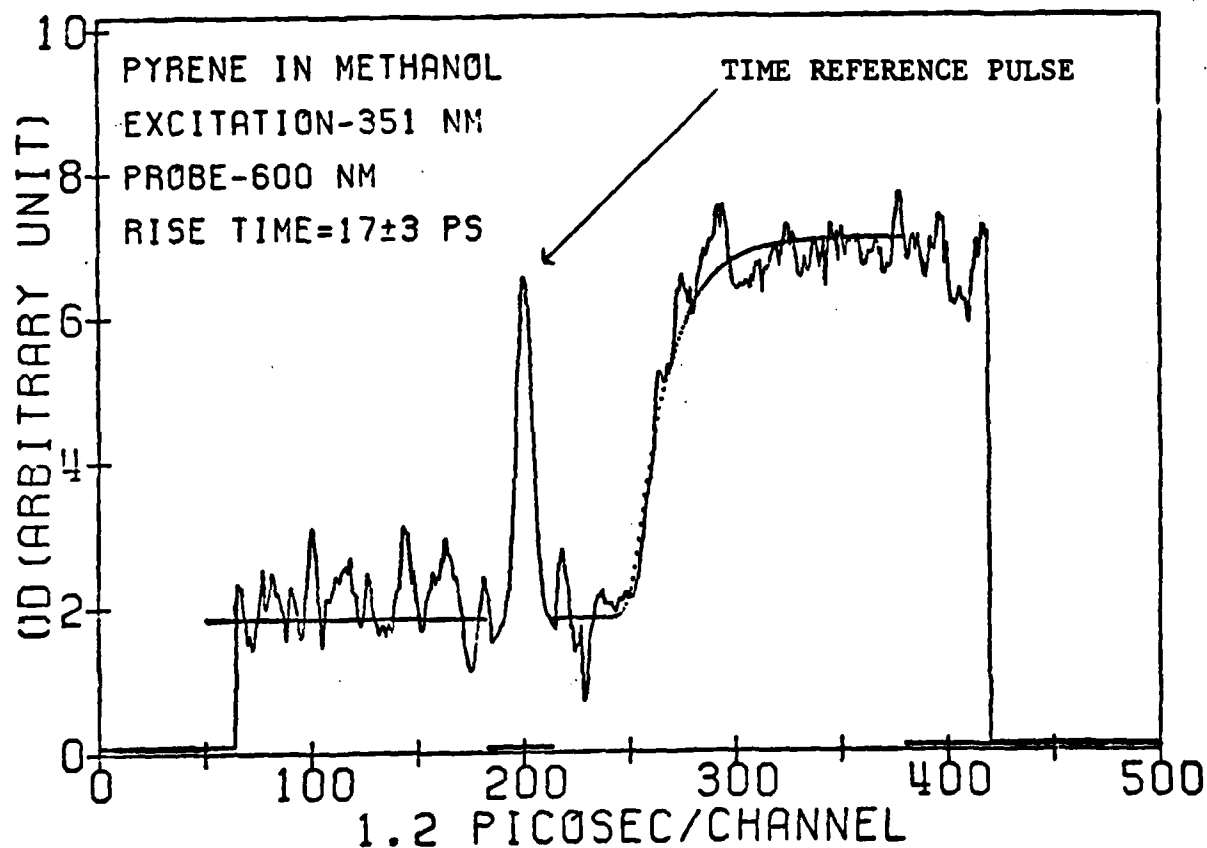
(and harmonics) as the excitation source, a picosecond streak camera serving as the detection system for either emission or the transient absorption of a laser triggered flash lamp, an optical multichannel analyzer for recording the time dependent optical signals, and finally a computer for data collection and manipulation.

To carry out transient absorption measurements covering nanoseconds or longer, but with picosecond resolution, we coupled a home-built laser triggered "white" light source with the picosecond streak camera. This transient absorption technique is quite different from the variable delay and transmission echelon techniques which utilize one or more laser probe pulses. These latter techniques require many laser shots at each time point, and many time points to yield the time-dependent absorption profile. In our method continuous time absorption is obtained in one laser shot with signal averaging capabilities by the easy use of a picosecond time marker.



PICOSECOND STREAK CAMERA - TRANSIENT ABSORPTION

The flash lamp has a rise time of less than 15 ns and an adjustable duration. The laser triggered feature solves a key problem in such a system, namely synchronization of the flash lamp pulse with the picosecond laser pulse used to excite the sample. An example of its use in our studies of electron solvation dynamics is shown below.



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